(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 448 157 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: 91200545.1

(51) Int. Cl.5: C07C 31/20, C07C 29/10

(22) Date of filing: 12.03.91

(30) Priority: 15.03.90 GB 9005814

(43) Date of publication of application:
25.09.91 Bulletin 91/39

(84) Designated Contracting States:
BE DE ES FR GB IT NL

(71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.
Carel van Bylandtlaan 30
NL-2596 HR Den Haag(NL)

(72) Inventor: Van Gogh, Johan
Badhuisweg 3
NL-1031 CM Amsterdam(NL)

(74) Representative: Tuijn, Jan Warnaar et al
Shell Internationale Research Maatschappij B.V., Patents, Licensing & Trade Marks Division, P.O. Box 302
NL-2501 CH The Hague(NL)

(54) **A two-step monoethylene glycol preparation process.**

(57) A two-step reaction process for converting ethylene oxide with high selectivity into monoethylene glycol which comprises firstly reacting ethylene oxide with acetone to 2,2-dimethyl-1,3-dioxolane and secondly hydrolyzing the 2,2-dimethyl-1,3-dioxolane with water to monoethylene glycol, both steps requiring the presence of a solid acid catalyst.

EP 0 448 157 A1

The invention relates to a two-step reaction process for converting ethylene oxide with high selectivity into monoethylene glycol.

It is generally known that monoethylene glycol is prepared by reaction of ethylene oxide with water at a temperature between 180 °C and 220 °C, wherein the amount of water is about 10 times the amount of ethylene oxide (by weight). Disadvantages of the process are that large amounts of water must be flashed off and still considerable amounts of diethylene glycol are prepared. The use of a catalyst may lead to a reduction in the amount of water (but not to stoichiometric amount), but the amount of diethylene glycol is hardly diminished.

Applicant has now found a process for the preparation of monoethylene glycol, which process does not have these disadvantages.

It is an object of the invention to prepare monoethylene glycol from ethylene oxide in very high yield.

It is another object of the invention to use as little water as possible.

According to the invention ethylene oxide is converted with high selectivity into monoethylene glycol in a two-step reaction process which comprises firstly reacting ethylene oxide with acetone to 2,2-dimethyl-1,3-dioxolane and secondly hydrolyzing the 2,2-dimethyl-1,3-dioxolane with water to monoethylene glycol, both steps requiring the presence of a solid acidic catalyst.

In the German "Auslegesschrift" 1,086,241 is disclosed the preparation of 1,3-dioxolanes by reacting epoxy compounds with carbonyl compounds in the presence of acid activated bentonite. The reaction between acetone and ethylene oxide has been mentioned and the yield of this step is 83 per cent. Reactions with other compounds give similar yields. The publication does not teach how the objects of our invention could be fulfilled.

In the UK Patent Application 2,098,985 is disclosed a two-step process whereby an alkylene oxide reacts with carbon dioxide in the presence of a phosphonium halide, there being substantially less than an equimolar amount of water present based on the ethylene oxide, to produce an alkylene carbonate, which latter product is reacted with water in the presence of the same phosphonium halide to a glycol. This two-step process has the disadvantages that rather high temperatures (180 °C) and no solid catalyst is used.

Solid acidic catalysts, to be employed in the process according to the invention are acid activated clays. They are especially suitable for the reaction of ethylene oxide with acetone into 2,2-dimethyl-1,3-dioxolane. Especially important clays are those of the montmorillonite series, such as montmorillonite, beidellite, nontronite, hectorite, saponite and sauconite. Acid activated clays are the clays which have been treated with mineral acids, such as hydrochloric acid or sulphuric acid. The acid activated clays are prepared by mixing crushed raw material with water to form a slurry to which the mineral acid amounting to about 35% of the total dry weight of the clay is added. The mixture is then treated with live steams for 5 to 8 hours, after which the whole mixture is dumped into fresh water and then washed, until it is substantially free of acids.

The mol ratio of acetone to ethylene oxide may range from 1:1 to 5:1, although higher ranges are not excluded.

Since the reaction of acetone with ethylene oxide is exothermic, the temperature is regulated by refluxing the acetone. At a later stage a somewhat higher temperature than the boiling temperature of acetone is suitable. The reaction temperature generally range from 30 °C to 80 °C, preferably from 50 °C to 65 °C.

In the hydrolyzing step either the raw mixture or purified 2,2-dimethyl-1,3-dioxolane may be used. Since 2,2-dimethyl-1,3-dioxolane boils at 92 °C, the compound can be purified by distillation. Hydrolysis of the 2,2-dimethyl-1,3-dioxolane in the second step is done in the presence of water with the aid of an acid activated clay or an ion-exchange resin. About the stoichiometric amount of water is sufficient to obtain substantial hydrolysis of the 2,2-dimethyl-1,3-dioxolane into monoethylene glycol and acetone. During this reaction the formed acetone is distilled off and any unreacted ketal may be recycled.

EXAMPLES

A. Preparation of the cyclic ketal 2,2-dimethyl-1,3-dioxolane

For the preparation of the ketal a glass, double walled reactor with a content of 2 litre was used provided with a glass stirrer and four glass joints for placing a thermocouple well, two gas inlet tubes and a reflux condenser. One of the gas inlet tubes was used for a slight nitrogen purge, the other one (both made from glass) being connected via a ball joint connection to the steel exit tube of a syringe pump (type LC-5000 from Isco Inc). containing the stock of liquid ethylene oxide under a pressure of 15-20 bar. Water was circulated around the wall of the glass reactor via a thermostatted bath for heating/cooling purposes.

The reactor was charged with 1695 ml (1340 g, 23.1 mol) of acetone and 34 g of K10 catalyst (acid activated montmorillonite, supplied by Sued-Chemie) and the suspension thus obtained was heated under stirring to 54 °C. At this stage the introduction of liquid ethylene oxide from the syringe pump was started, an amount of 305 ml (269 g, 6.1 mol) being introduced in the course of 45 minutes. By means of a valve in the steel exit tube of the Isco pump a pressure in the latter of 15-20 bar was maintained to keep the ethylene oxide in the liquid form. At 54 °C the formation of the cyclic ketal started immediately, the heat of reaction being removed via refluxing of the excess of acetone; the boiling point of reaction mixture gradually increased over the period of ethylene oxide addition (due to formation of the cyclic ketal, bp. 92 °C) from 56 °C to 62 °C.

After a post reaction of 15 minutes the reaction mixture was cooled and the K10 catalyst allowed to settle after which the supernatant liquid was sucked by slight vacuum from the catalyst layer. Then a new batch of acetone was charged to the reactor and the reaction repeated, the amounts of acetone and ethylene oxide being the same as described above with the original amount of K10 catalyst, which was thus reused.

Twelve batch reactions were carried out according to the procedure described above. The combined product (18.42 kg) in which no ethylene oxide could be detected had the following composition (GC analysis):

acetone :	60.7 %w
ketal :	38.9 %w
monoethyleneglycol :	0.1 %w
diethyleneglycol :	0.2 %w
1,4-dioxane :	0.1 %w

B. Hydrolysis of the cyclic ketal

Two options were carried out by addition of water and acid catalyst either to the reaction mixture prepared under A or to the ketal isolated prior to the hydrolysis step.

The equipment used was a 10 l distillation flask provided with a fractionating Vigreux column of approx. 6 m length having 15-20 theoretical plates.

1. Hydrolysis of the reaction mixture

Into the distillation flask were present the following components: reaction mixture prepared

according to method under A:	6000 g
water :	452 g water/ketal mol ratio 1.09
Amberlyst 15 :	10 g

The acid ion exchange resin catalyst Amberlyst 15 (styrene-divinylbenzene copolymer containing sulphonic acid groups) was wrapped in glass cloth and placed into the distillation flask in order to prevent crushing during boiling of the reaction mixture. The excess of acetone as well as the amount of acetone from the hydrolysis of the ketal was distilled at atmospheric pressure. When the bulk of the ketal had been converted into glycol and acetone the boiling point started to rise sharply but was maintained at 110 °C to protect the catalyst. Further conversion of the ketal was then carried out under a pressure of 250 mbar until distillation of the acetone stopped. The following mass balance was obtained:

	In (g)	Out (g)
ketal	: 2352 (23.1 mol)	31.8 (0.3 mol)
monoethylene glycol:	17.4 (0.3 mol)	1414.7 (22.8 mol)
total mass	: 6452	6445

Thus, the total mass balance was 99.9% and the mol balance of MEG + ketal 98.7%.

This result points to a catalyst consumption of less than 1% by weight on monoethylene glycol.

2. Hydrolysis of the cyclic ketal isolated from the reaction mixture

An amount of 5212 g of the reaction mixture (prepared according to method under A) was distilled in

order to isolate the bulk of the ketal. A distilled fraction of 2036 g containing 89.6 %w ketal (17.88 mol), 10.3 %w acetone and about 0.2 %w 1,4-dioxane was combined with 355 g H_2O (mol ratio H_2O/ketal 1.1) and 20 g of Amberlyst 15 (wrapped in glass cloth). Because the liquid mixture consisted of two phases, it was homogenized at room temperature by a shift of equilibrium before being introduced with the catalyst in the distillation flask.

Equilibration and distillation of the acetone (basically the same procedure as applied in the first hydrolysis under 1) yielded ultimately a residue containing 1091 g monoethylene glycol (17.6 mol) and traces of acetone, unconverted ketal and 1,4-dioxane but no heavy glycols. The mol balance on monoethylene glycol and total unconverted ketal (0.12 mol) was 99%, the same figure being found for the total mass balance.

Claims

1. A two-step reaction process for converting ethylene oxide with high selectivity into monoethylene glycol which comprises firstly reacting ethylene oxide with acetone to 2,2-dimethyl-1,3-dioxolane and secondly hydrolyzing the 2,2-dimethyl-1,3-dioxolane with water to monoethylene glycol, both steps requiring the presence of a solid acid catalyst.

2. A process as claimed in claim 1, wherein the catalyst used in the first step is an acid activated clay.

3. A process as claimed in claim 1 or 2, wherein the mole ratio of acetone/ethylene oxide ranges from 1:1 to 5:1.

4. A process as claimed in one or more of the claims 1-3, wherein the reaction temperature ranges from 30 °C to 80 °C.

5. A process as claimed in one or more of the claims 1-4, wherein the 2,2-dimethyl-1,3-dioxolane is distilled off.

6. A process as claimed in one or more of the claims 1-5, wherein the 2,2-dimethyl-1,3-dioxolane is hydrolyzed with water in the presence of an ion-exchange resin or an acid activated clay.

7. A process as claimed in claim 6, wherein a substantially stoichiometric amount of water is used for the hydrolysis of 2,2-dimethyl-1,3-dioxolane in monoethylene glycol and acetone.

8. A process as claimed in claim 6 or 7, wherein the acetone is distilled off during the reaction.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91200545.1

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,Y	DE - C - 1 086 241 (CHEMISCHE WERKE HÜLS) * Column 1, lines 15-54 * --	1-4	C 07 C 31/20 C 07 C 29/10
Y	PATENT ABSTRACTS OF JAPAN, unexamined application, C field, vol. 8, no. 168, August 3, 1984 THE PATENT OFFICE JAPANESE GOVERNMENT page 79 C 236 * Kokai-no. 59-67 233 (KOGYO GIJUTSUIN) * --	1,5-8	
A	US - A - 4 568 780 (JOHN F. KNIFTON) * Abstract * --	1	
A	US - A - 4 609 768 (JOHN F. KNIFTON et al.) * Abstract * --	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
D,A	GB - A - 2 098 985 (IMPERIAL CHEMICAL INDU-STRIES) * Abstract * --	1	C 07 C 31/00 C 07 C 29/00
A	US - A - 4 400 559 (VIJAY S. BHISE) * Abstract * ----	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	17-06-1991	REIF

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document